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Cycloisomerization

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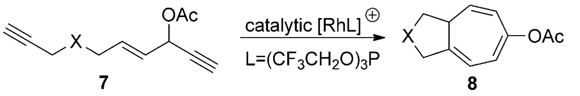
Interception of a Rautenstrauch Intermediate by Alkynes for [5+2] Cycloaddition: Rhodium-Catalyzed Cycloisomerization of 3-Acyloxy-4-ene-1,9-diynes to Bicyclo[5.3.0]decatrienes**

*Xing-zhong Shu, Suyu Huang, Dongxu Shu, Ilia A. Guzei, and Weiping Tang**

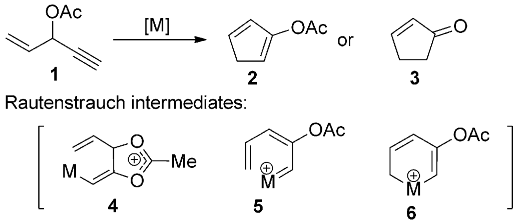
Dedicated to Professor Barry M. Trost on the occasion of his 70th birthday

In 1984, Rautenstrauch reported that the 3-acyloxy-1,4-enyne **1** could undergo cyclization to form cyclopentadiene **2** and cyclopentenone **3** in the presence of a palladium catalyst through 1,2-acyloxy migration (Scheme 1).[1] The vinyl metal complex **4**, metal carbene **5**, and metallacyclohexadiene **6** were proposed as intermediates in this transformation.[1,2] The scope of this rearrangement reaction has been expanded significantly by the use of π-acidic metals,[3] such as gold- and platinum-based catalysts, for the synthesis of functionalized five-membered rings.[4] The 1,2-acyloxy migration of propargyl esters has also been employed in other synthetically useful transformations catalyzed by gold,[5,6] platinum,[6,7] ruthenium,[8,9] copper,[6] and more recently rhodium.[10]

We recently found that $[\{Rh(CO)_2Cl\}_2]$ was able to catalyze the 1,3-acyloxy migration of propargyl esters in the synthesis of functionalized cyclohexenones.[11] The combination of this novel reactivity of Rh^I in promoting acyloxy migration and its well-known capability to undergo facile oxidative addition, migratory insertion, and reductive elimination may offer many opportunities for the design of new reactions. We envisioned that a conceptually new approach to seven-membered rings was possible if intermediate **6** in the Rautenstrauch rearrangement could be intercepted by a tethered alkyne in a [5+2] cycloaddition under rhodium catalysis.[12–16] We herein report a new atom-economical[17] synthesis of a bicyclo[5.3.0]decatriene **8** through a rhodium(I)-catalyzed cycloisomerization[18] of a 3-acyloxy-4-ene-1,9-diyne **7** [Eq. (1)]. The net result of this reaction is an intramolecular [5+2] cycloaddition[14–16] with concomitant 1,2-acyloxy migration. The resulting complex bicyclo[5.3.0]decane skeletons are present in many natural products.[19]



(1)



Scheme 1. Rautenstrauch rearrangement.

Besides the Rautenstrauch rearrangement to form five-membered rings, a number of other pathways may also compete with the desired cycloisomerization of enyne **7** to the bicyclic compound **8**. For example, if a carbene intermediate similar to **5** is generated, it may undergo cyclopropanation or cyclopropenation with alkenes or alkynes in the system. However, when substrate **7a**, available in four steps from 2-butene-1,4-diol,[20] was treated with a catalytic amount of $[\{Rh(CO)_2Cl\}_2]$, cycloisomerization occurred to give the bicyclic product **8a** in 19 and 48% yield in toluene and dichloroethane (DCE), respectively (Table 1, entries 1 and 2). Several other Rh^I catalysts also promoted this reaction (Table 1, entries 4–6). The cationic Rh^I catalyst $[Rh(cod)_2]BF_4$ promoted the tandem cycloisomerization even at room temperature (Table 1, entry 6). The reaction is solvent-dependent (Table 1, entries 7 and 8), and higher yields were generally observed with chlorinated solvents (entries 9 and 10). A complex 5,7-fused bicyclic compound can thus be prepared in a single step from a readily available linear 3-acyloxy-4-ene-1,9-diyne under rhodium catalysis. Au^I, Pt^{II}, or Brønsted acid catalysts did not provide any of the desired product (Table 1, entries 11–13).

We next examined the scope of this tandem cycloisomerization under conditions A (Table 2). The reaction remained efficient when the ester was changed from a pivalate to an acetate or benzoate (Table 2, entries 1–3). Substrates with a nitrogen or a *gem*-diester linker in the 1,6-enyne yielded bicyclic compounds **8d** and **8e** successfully (Table 2, entries 4 and 5). The structure of bicyclic product **8d** was assigned unambiguously by X-ray crystallographic analysis.[21]

We systematically examined the scope of this rhodium(I)-catalyzed cycloisomerization by placing substituents at differ-

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[*] Dr. X-z. Shu, S. Huang, Prof. Dr. W. Tang
The School of Pharmacy, University of Wisconsin
Madison, WI 53705-2222 (USA)
E-mail: wtang@pharmacy.wisc.edu
Homepage: https://mywebspace.wisc.edu/wtang5/web/
D. Shu, I. A. Guzei
Department of Chemistry, University of Wisconsin (USA)

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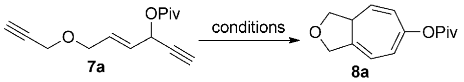
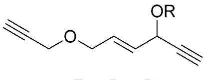
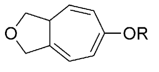
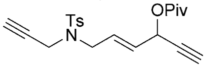
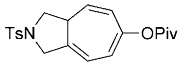
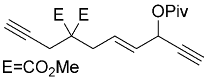
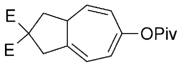
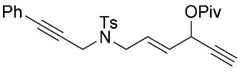
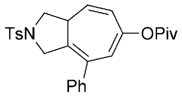
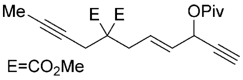
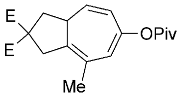
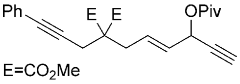
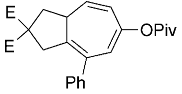
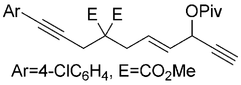
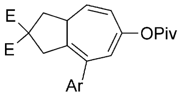
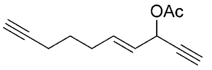
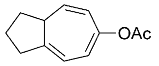
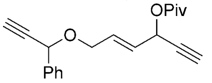
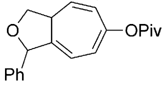
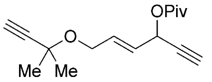
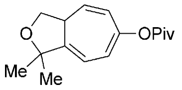
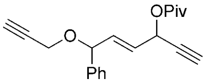
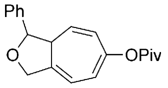
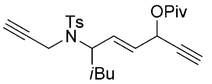
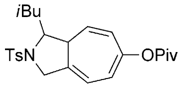
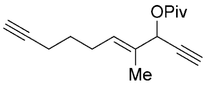
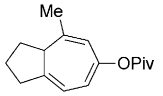
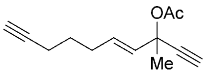
Table 1: Screening of catalysts and conditions for rhodium(I)-catalyzed cycloisomerization.



Entry	Conditions	Yield [%][a]
1	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%), toluene, 90°C, 8 h	19
2	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%), DCE, 90°C, 8 h	48
3	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%), TCE, 90°C, 1.5 h	43
4	$[\{Rh(cod)Cl\}_2]$ (5 mol%), TCE, 90°C, 8 h	21
5	$[Rh(PPh_3)_3Cl]$ (5 mol%), TCE, 90°C, 8 h	77
6	$[Rh(cod)_2]BF_4$ (5 mol%), DCE, RT, 8 h	70
7	$[Rh(cod)_2]BF_4$ (5 mol%), toluene, RT, 8 h	n.r.
8	$[Rh(cod)_2]BF_4$ (5 mol%), dioxane, RT, 8 h	n.r.
9	$[Rh(cod)_2]BF_4$ (5 mol%), TCE, 50°C, 20 h	81
10	$[Rh(COD)_2]BF_4$ (5 mol%), CH_2Cl_2, RT, 8 h	83
11	$[AuCl(PPh_3)]$ (5 mol%), AgOTf (5 mol%), MeCN, RT, 20 h	0
12	$PtCl_2$ (10 mol%), DCE, 80°C, 20 h	0
13	$HNTf_2$ (10 mol%), CH_2Cl_2, RT, 20 h	0

[a] The yield was calculated on the basis of ^1H NMR spectroscopy with an internal standard. cod = 1,5-cyclooctadiene, n.r. = no reaction, Piv = pivaloyl, TCE = tetrachloroethane, Tf = trifluoromethanesulfonyl.

Table 2: Scope of the rhodium(I)-catalyzed cycloisomerization.

Entry	Substrate	Product	Yield [%][a] (cond.[b])
			
1	**7a**, R = Piv	**8a**, R = Piv	85 (A)
2	**7b**, R = Ac	**8b**, R = Ac	81 (A)
3	**7c**, R = Bz	**8c**, R = Bz	83 (A)
4	 **7d**	 **8d**	96 (A)
5	 **7e**	 **8e**	75 (A)
6	 **7f**	 **8f**	88 (B)
7	 **7g**	 **8g**	82 (B)
8	 **7h**	 **8h**	70 (B)
9	 **7i**	 **8i**	60 (B)
10	 **7j**	 **8j**	76 (B)
11	 **7k**[c]	 **8k**[c]	90 (A)
12	 **7l**	 **8l**	90 (A)
13	 **7m**[c]	 **8m**[c]	76 (B)
14	 **7n**[c]	 **8n**[c]	80 (B)
15	 **7o**	 **8o**	80 (B)
16	 **7p**	complex mixture	(A or B)

[a] Yield of the isolated product. [b] Conditions A: $[Rh(cod)_2]BF_4$ (3–5 mol%), CH_2Cl_2 (0.05 M), RT or 50°C, 8–48 h; conditions B: $[Rh(cod)_2]BF_4$ (5–10 mol%), $(CF_3CH_2O)_3P$ (10–20 mol%), CH_2Cl_2 (0.025–0.05 M), 50°C, 8–24 h. [c] The diastereomeric ratio is 1:1. Bz = benzoyl, Ts = *p*-toluenesulfonyl.

ent positions on the 1,9-diyne. For substrates **7f**–**7i** with an internal alkyne on the left-hand side, either no reaction or only a trace amount of the product was observed under conditions A. We then explored the effect of ligands on the cycloisomerization of substrate **7f** with the $[Rh(cod)_2]BF_4$ catalyst. The addition of PPh_3, iBu_3P, or 1,2-bis(diphenylphosphanyl)ethane (dppe) had no effect. Triethyl phosphite improved the conversion of substrate **7f** to 21% according to ^1H NMR spectroscopy. Similar conversion was also observed with the electron-poor phosphine ligands $(C_6F_5)_3P$ and $(p\text{-}CF_3C_6H_4)_3P$. The electron-poor phosphite ligand $(CF_3CH_2O)_3P$ significantly improved the conversion: substrate **7f** was completely consumed within 8 hours, and product **8f** was isolated in 88% yield (Table 2, entry 6). A novel catalytic system composed of cationic Rh^I and tris(2,2,2-trifluoroethyl) phosphite was thus developed (conditions B).

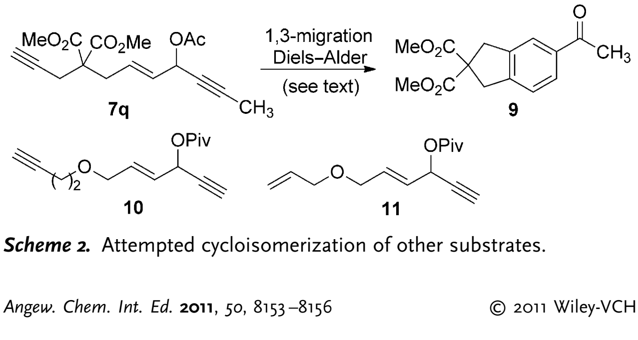
Dramatic improvements were also observed for other substrates with internal alkynes when a combination of the catalyst $[Rh(cod)_2]BF_4$ and the ligand $(CF_3CH_2O)_3P$ was used (Table 2, entries 7–9). The all-carbon tether was not limited to substrates with *gem*-diester substituents. Moderate conversion (40–50%) was observed for substrate **7j** when the catalyst $[Rh(cod)_2]BF_4$ (3–10 mol%) was used alone. Again, the addition of the ligand $(CF_3CH_2O)_3P$ improved the yield of product **8j** (Table 2, entry 10).

We then examined the effects of substituents in the tether region. Substituents adjacent to the left-hand alkyne had no apparent effect, and the cycloisomerization proceeded efficiently under conditions A (Table 2, entries 11 and 12). We were very pleased to find that the reaction even tolerated the quaternary carbon center adjacent to the reacting alkyne in substrate **7l**. Substituents adjacent to the alkene, however, lowered the conversion, and the addition of $(CF_3CH_2O)_3P$ as a ligand was necessary for the formation of the product in good yield (Table 2, entries 13 and 14). A trisubstituted olefin was also tolerated: the bicyclic product **8o** was obtained in good yield (Table 2, entry 15). However, when a substrate with a tertiary ester was subjected to conditions A or B, a complex mixture was formed (Table 2, entry 16).

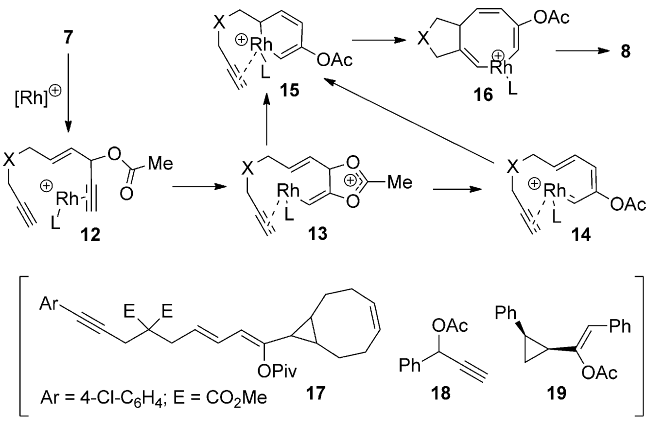
For substrates with an internal alkyne at the right-hand end (e.g. **7q**, Scheme 2), the formation of benzene derivatives (e.g. **9**) in the presence of a $PtCl_2$ catalyst has been reported.[22] A 1,3-acyloxy migration followed by a Diels–Alder-type reaction was proposed for this transformation. When we treated **7q** with the cationic Rh^I catalyst, a trace amount of product **9** was observed, and the starting material was mainly recovered. We have previously shown that $[\{Rh(CO)_2Cl\}_2]$ is an efficient catalyst for the 1,3-acyloxy migration of propargyl esters.[11] Indeed, our preliminary study showed that product **9** could be obtained in 30–40% yield with the catalyst $[\{Rh(CO)_2Cl\}_2]$. Since this transformation has been carried out with the catalyst $PtCl_2$, no further optimization was conducted. These results, however, did show that the 1,2- and 1,3-acyloxy migration of propargyl esters is dependent on the nature of the substrate and the Rh^I catalyst, and are thus consistent with observations made with other metal catalysts.[3]

Substrates with six-atom or longer tethers between the two reactive π systems are often challenging in transition-metal-catalyzed intramolecular cycloaddition and cycloisomerization reactions.[18] Substrate **10** (Scheme 2) was prepared to test the limits of the present cycloisomerization. Under standard conditions A or B, no reaction occurred, and the starting material was recovered. A tethered alkene also failed to intercept the Rautenstrauch intermediate: when the 3-acyloxy-substituted dienyne **11** was subjected to conditions A or B, the starting material was recovered.

We propose a mechanism involving a Rautenstrauch intermediate for the formation of products **8** from enediynes **7** (Scheme 3): A rhodium(I)-promoted 1,2-acyloxy migration of the propargyl ester in complex **12** provides a vinyl metal species **13**. The metallacyclohexadiene **15** may be formed through the direct cyclization of intermediate **13**, or via carbene **14** through a 6 π electrocyclization. Insertion of the tethered alkyne into the metallacycle **15**, followed by reductive elimination of the metallacyclooctatriene **16**, then produces product **8** with a seven-membered ring.[18] As the yield for the transformation of substrate **7i** into product **8i** was the lowest observed for the successful reactions in this study (Table 2, entry 9), we carefully analyzed the by-products of this reaction. We isolated a small amount of cyclopropane **17** (Scheme 3), which was presumably derived from the reaction between a Rh^I carbene and one of the cyclooctadiene ligands in the catalyst. Compound **17** became the major product when excess external cyclooctadiene (2.0 equiv) was added to the reaction mixture. However, when the external cyclooctadiene was replaced by the same amount of styrene, no cyclopropanation product derived from styrene was observed. This difference may be attributed to the bidentate nature of cyclooctadiene. When we treated propargyl ester **18** with the different Rh^I catalysts in Table 1 in the presence of styrene, the known cyclopropane **19**[8] was isolated in several cases. This outcome again suggested the formation of a Rh^I carbene from the propargyl ester. Although there are other potential mechanisms, the above results are consistent with the mechanism proposed in Scheme 3 based on the interception of a Rautenstrauch intermediate by an alkyne.



Scheme 2. Attempted cycloisomerization of other substrates.



Scheme 3. Proposed mechanism for the rhodium(I)-catalyzed cycloisomerization and evidence for the involvement of a rhodium(I) carbene.

In summary, we have developed a conceptually novel intramolecular [5+2] cycloaddition with concomitant 1,2-acyloxy migration for the synthesis of highly functionalized seven-membered rings. Various substituted bicyclo[5.3.0]decatrienes were synthesized in this way from readily available linear starting materials. The cycloheptatriene in the resulting bicyclic system has three well-differentiated double bonds ready for further functionalization.[19] Cycloheptatrienes themselves are also widely present in polycyclic natural products and pharmaceutical agents.[23] Further studies to uncover the details of the mechanism, expand the scope of the reaction, and apply this novel cycloisomerization to the synthesis of natural products and pharmaceutical agents are currently in progress.

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Keywords: alkenynes · cycloaddition · cycloisomerization · polycycles · rhodium

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[2] V. Rautenstrauch, *Tetrahedron Lett.* **1984**, *25*, 3845.
[3] For reviews on π-acidic-metal-catalyzed reactions, see: a) K. Miki, S. Uemura, K. Ohe, *Chem. Lett.* **2005**, *34*, 1068; b) N. Marion, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 2806; *Angew. Chem. Int. Ed.* **2007**, *46*, 2750; c) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478; *Angew. Chem. Int. Ed.* **2007**, *46*,

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